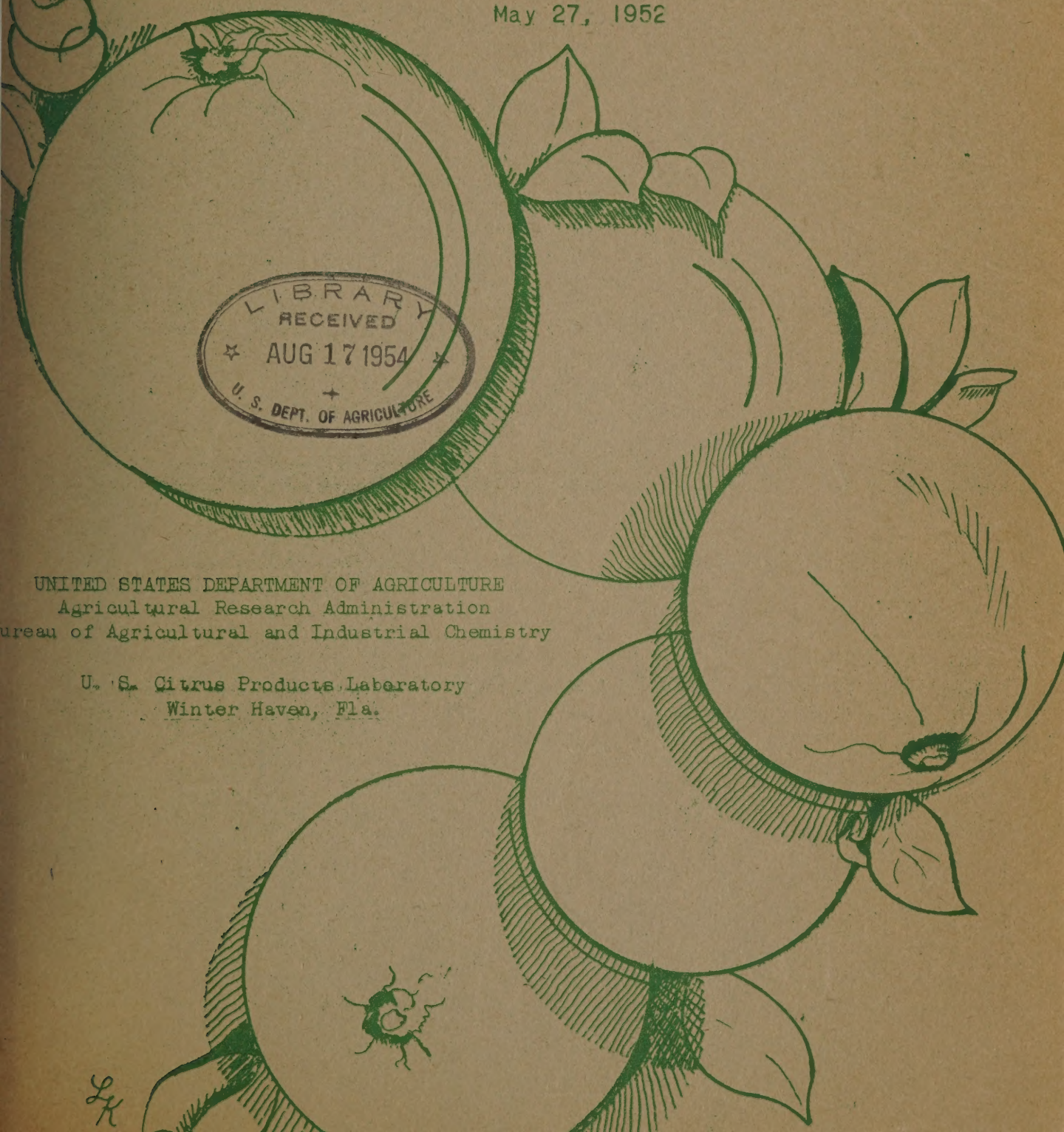
Citrus PROCESSING CONFERENCE

May 27, 1952



UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Administration
Bureau of Agricultural and Industrial Chemistry

U. S. Citrus Products Laboratory
Winter Haven, Fla.

PROGRAM AND ABSTRACTS OF PAPERS

CONFERENCE ON CITRUS PROCESSING

May 27, 1952

at the

Florida Room, Citrus Building
Winter Haven, Florida

FOREWORD

The Conference on Citrus Processing held May 9, 1951, in Winter Haven, was so highly successful in facilitating the exchange of information between the representatives of industry and of federal and state research agencies, that it was decided to hold another in 1952. In the interim, citrus research has progressed and the citrus processing industry has expanded. Processed products are assuming an ever increasing role in the utilization of the citrus crops of the nation. Close industry-research cooperation is essential. The industry should be promptly informed of research developments in order that these may be applied to improving the quality and quantity of its old and new food, feed, and chemical products. A conference affords a convenient means of exchanging this information.

Like the preceding one, the 1952 conference has been arranged by the Bureau of Agricultural and Industrial Chemistry of the U. S. Department of Agriculture through its field office, the U. S. Citrus Products Laboratory in Winter Haven 1/, in cooperation with the Technical Advisory Committee, the Citrus Products Research Council, the Citrus Experiment Station, the Florida Canners Association and the Florida Section of the Institute of Food Technologists.

A program and abstracts of the papers to be presented compose this report. For additional information on any subject covered, please contact the author or organization concerned.

1/ One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Administered by the Southern Regional Research Laboratory, New Orleans, Louisiana.

CONFERENCE ON CITRUS PROCESSING
Florida Room, Citrus Building
Winter Haven, Florida
May 27, 1952

MORNING SESSION

Chairman: John R. Matchett
Asst. Chief
Bur. of Agric. & Ind. Chem.
Washington, D. C.

AFTERNOON SESSION

Chairman: M. K. Veldhuis
In Charge
U. S. Citrus Products Laboratory
Winter Haven, Florida

REVIEW OF CITRUS RESEARCH PROGRAM OF FRUIT AND
VEGETABLE CHEMISTRY LABORATORY
PASADENA, CALIFORNIA
E. A. Beavens

Nitrogenous Constituents in Citrus Juices

by

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Fruit and Vegetable Chemistry Laboratory
Pasadena, California

It has been shown by other workers that interactions between nitrogenous compounds, carbohydrates, ascorbic and citric acids in citrus juices and ad hoc mixtures favor the development of off-flavors and darkening in processed products. Due in part to the unavailability of suitable analytical procedures, little has been known about the character of the nitrogenous constituents which compose almost 10 percent of the total solids in citrus juices.

Using newly developed filter paper chromatography techniques, it has been possible to identify most of the major nitrogenous constituents in Valencia and Navel orange, grapefruit, lemon, lime and tangerine juices. Orange juice appears to contain a larger array of free amino acids than was found with the other juices, and each of the citrus juices contains characteristic types and amounts of these constituents.

Using improved chromatography techniques, several new nitrogenous constituents have been found in the juice of mature Valencia oranges. These compounds, which have not been fully identified, are of particular interest because they are present only in the juice of the mature fruit. In addition, several other unidentified nitrogenous compounds have been detected only in the juice of immature oranges.

Preliminary experiments indicated that the amounts of free amino acids in orange juice may vary with the maturity of the fruit. For example, one study showed that with Valencia oranges arginine and an unknown basic nitrogen compound increased in amount as the season progressed. On the other hand, asparagine and another unknown constituent decreased as the fruit matured. Also, several unidentified nitrogenous compounds were present only in very immature fruit. Quantitative measurements will be made to determine the relationship between the concentrations of the various amino acids and the sugar-acids ratios of the same juices to provide a basis for a new maturity test.

Quantitative filter-paper chromatography methods have been applied to fresh and heated juices of orange, grapefruit, lemon and lime for the determination of the two sulfur-containing nitrogenous compounds cysteine and glutathione. Significant losses of both of these compounds occurred after heating. Three additional compounds, which appear to contain sulfhydryl-sulfur, have been detected on filter paper chromatograms of concentrates of fresh and heated lemon, lime, and grapefruit but not orange juices.

A study will be initiated on the effect of previously identified nitrogen and sulfur-containing compounds on the formation of undesirable colors, flavors, and odors during the processing and storage of citrus juices.

Publication:

Nitrogenous Constituents of Citrus Fruit Juices. L. B. Rockland, J. C. Underwood, and E. A. Beavens. Calif. Citrograph 35(11):490-492, Sept., 1950.

Volatile Flavoring Constituents of Citrus Fruits

by
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A new method of chromatography has been developed for use in the separation and identification of terpenes, the main flavoring constituents of citrus fruits. The technique consists in plating an adsorbent mixed with a suitable binder on glass strips (1/2 x 5-1/4 inches). Chromatography of the terpenes is then carried out in the same manner as filter paper chromatography. The method is very sensitive and as little as 0.3 microgram of some compounds can be detected. Unique color tests were originated in order to locate various compounds. These tests also give indications of the structure of the compound. For example, ethylenic type double bonds, aldehydes, acids, benzene type structures, etc., are indicated by the various reagents.

The value of these new methods has been demonstrated on oils obtained from grapefruit juice. The fractions obtained by fractional distillation of the oil from grapefruit were examined chromatographically. The complexity of these fractions showed that fractional distillation could not be relied on to sharply separate the components from the small amounts of oil available.

From fresh grapefruit juice five compounds have been isolated which appear to be single compounds as judged by chromatography in five different solvents. A compound containing nitrogen and having a grape-like odor has been proved to be neither ethyl nor methyl anthranilate. It may be N-methyl methyl anthranilate.

Two compounds have been isolated in purified form from canned juice fractions, a $C_{10}H_{18}O_2$ and a $C_{10}H_{18}O$ compound.

Five additional compounds have been isolated in pure form from the oil of fresh grapefruit juice, making a total of ten compounds isolated to date. Empirical formulas have been established for seven of these compounds and physical constants have been determined for a majority of them. Twelve compounds have been isolated from the oil of freshly canned grapefruit juice. Five have been definitely identified, two have been tentatively identified, and empirical formulas have been established for four others. A fraction composed of polymers of highly oxygenated compounds has been isolated.

Chromatographic studies using the chromatostrip method have led to the development of a new method for separating terpenes from non-terpenes in essential oils. It has been demonstrated that a mixture of hydrocarbons (terpenes) and oxygen substituted hydrocarbons (non-terpenes) can be completely separated by a silicic acid adsorbent. Using this principle several essential oils including orange, grapefruit, and lemon have been deterpened. Physical and chemical data have been obtained on several oils to indicate the completeness of removal of the terpenes, and to characterize the deterpened oils. The process has possible commercial application.

Publications:

A New Type of Chromatographic Column. J. M. Miller and J. G. Kirchner. Analyt. Chem. 23(3):428-430, Mar., 1951.

Separation and Identification of 2,4-Dinitrophenylhydrazones of Aldehydes and Ketones, and 3,5-Dinitrobenzoates of Alcohols by Filter Paper Chromatography. R. G. Rice, J. G. Kirchner, G. J. Keller. Analyt. Chem. 23(1): 194-195, Jan., 1951.

Separation and Identification of Terpenes by a New Chromatographic Technique. J. G. Kirchner, J. M. Miller and G. J. Keller. Analyt. Chem. 23(3):420-425, Mar., 1951.

What Gives Fruit a Flavor? J. G. Kirchner. U. S. Department of Agriculture Yearbook, Crops in Peace and War, pp. 251-255, 1950-51.

A New Method for the Preparation of Terpeneless Essential Oils. J. G. Kirchner and J. M. Miller. Ind. Eng. Chem. 44(2):318-321, Feb., 1952.

Microbiology of Citrus Products

by
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Fruit and Vegetable Chemistry Laboratory
Pasadena, California

Studies have been continued to determine the source of contamination, incidence and sanitary significance of coliform organisms found in citrus products. Examinations were made of freshly picked fruit, fruit from packing houses, fruit and juices from processing plants, and stored frozen concentrates. Surface contamination of packing house and processing plant equipment was studied also.

Escherichia coli organisms were not found on the surface of oranges aseptically harvested from nine groves during the 1951 season. However, on occasions other coliform species were isolated from similar fruit. A low index of *E. coli* (one cell per 37 cm^2 of fruit surface) was recovered from at least one sample of packing house fruit. *Aerobacter* and *E. freundii* strains were found on other samples of packing house fruit.

E. coli organisms were recovered more frequently from samples obtained from concentrate plants. For example, they were recovered from fruit taken from unloading trucks, storage bins, washed fruit and from extractors. When water in the wash tanks was adequately chlorinated, no E. coli were found on washed fruit. A sample of unchlorinated wash water contained 15 E. coli organisms per ml.

E. coli was recovered on several occasions from each of the following points in citrus concentrate plants: juice from extractors, evaporator feed juice, cut back juice, 55° Brix concentrate and the final 43° Brix concentrate. In contrast to the 1950 season, when the E. coli index for similar samples was usually below 5 cells per 100 ml., the index for the 1951 season was above 10 cells per 100 ml. in two-thirds of the samples containing E. coli. The presence of softer fruit during the past season may have accounted for this increased incidence. In past seasons it was observed that E. coli was more prevalent in the soft, late season fruit.

Surface checks of plant equipment showed that fruit storage bins are frequently contaminated with E. coli. Over half of the swab tests made from bin surfaces were E. coli positive. Truck beds, elevators, conveyor belts and unchlorinated wash tanks were also found to harbor this bacterium.

In storage studies E. coli was found to survive up to two years in one lot of frozen orange concentrate containing a high initial coli index. During storage at 0° to -10° F. the index dropped from 540 to 7 cells per 100 ml. In other lots of stored frozen concentrate having lower coli indices the organisms disappeared in much shorter times.

Comparative studies have been in progress on the use of boric acid broth versus standard lactose broth as presumptive media for the isolation of E. coli from citrus products. Parallel tests run on 2,271 tubes of each medium indicated the boric acid broth gave best results.

Time-Temperature Tolerance Studies

by
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During the past year studies were initiated on the time-temperature tolerance of frozen citrus concentrates.

Three large lots of commercial frozen orange concentrate obtained from different plants in this area are now undergoing storage tests that simulate the time-temperature conditions which may be encountered in storage and distribution, including freighting, warehousing, retail handling and consumer use. Both normal and abnormal conditions of temperature have been employed during simulated freight and retail handling. Samples are carried over from one temperature history to all subsequent temperature conditions. In this manner the cumulative as well as the immediate effects of a particular temperature history are being investigated.

Additional studies will be made of the effect of temperature of storage at constant temperature and of the effect of very slow recooling from elevated temperatures as might occur when samples, warmed during shipment, are closely stacked in commercial warehouses.

The principal physical and chemical changes under study are: pectic substances in conjunction with "cloud-loss", pectic enzymes, titratable acidity, ascorbic acid and carotene. Microbiological studies are made of variations in total count and coliform counts. Flavor evaluation is made by triangular taste-testing covered in a separate abstract.

Preliminary evidence indicates that most chemical factors undergo little change during storage. The stability of "cloud" in orange concentrate decreases with length of storage, and brief exposure to temperatures above 20° F. causes abrupt losses in "cloud". The pectic changes associated with "cloud-loss" appear to be complex in nature and much additional information must be gathered before a clear understanding of these changes and their mechanism will be possible.

Flavonoid Constituents in Citrus Fruits

by
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Pasadena, California

During the past year research on flavonoid constituents has been concerned chiefly with the development of satisfactory procedures for the identification and separation of known purified flavonoids and related substances using one and two dimensional chromatographic techniques. As improved methods were perfected for the determination of known compounds they were applied to the analysis of juices and tissues of citrus fruits to gain a knowledge of their flavonoid composition.

One important result of the work on pure flavonoids, which involved the testing of many solvents, staining reagents, and substances capable of dissolving flavonoids without decomposing them, was the development of a method for separating pure flavonoids into calsses. This was an important development since the number of naturally occurring flavonoids is very large.

Using these improved chromatographic techniques naringin and hesperidin have been the only flavonoids positively identified in citrus fruits. However, investigations have shown that a number of unidentified flavonoid-like compounds are also present in citrus fruits. In general, the juice and flavedo contained more of these compounds than were found in the albedo, although those found in the albedo were present in larger quantities. Green fruits appeared to contain the largest numbers and amounts of flavonoid substances. Results so far obtained indicate as many as ten flavonoid-like substances may be present in citrus fruits. It will be necessary to isolate the individual flavonoids in sufficient quantities to permit studies of their chemical characteristics and to determine their effect on the quality of processed citrus juices. Results of preliminary chromatographic work on pure flavonoids will aid greatly in this work.

Past studies have been concerned largely with grapefruit and oranges. However, since lemon products are becoming increasingly important in Southern California, and the darkening of these products has been attributed to the action of flavonoid substances, future studies will be directed toward a solution of this important problem.

Flavor Fortification and Production of High Density Citrus Concentrates

by

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Previously reported investigations demonstrated that the volatile flavor and aroma of orange juice are due principally to essential oils, and it is the loss of these oils during evaporation that causes a concentrate to be deficient in flavor. It was shown that when cut-back juice is used to restore flavor and aroma to concentrates it does so because it contains relatively large amounts of these oils, and that when large amounts of oil are present in juice it is primarily derived from the peel of the fruit. It was successfully demonstrated, therefore, that peel oil itself, or materials rich in peel oil such as puree, could be used to restore flavor and aroma to concentrates in place of cut-back juice. The use of peel oil was shown to offer not only the advantages of improved flavor control and increased production, but since these materials do not dilute the product, higher concentrations than the conventional 4 to 1 fold were possible.

During the past season higher concentrations of 5 to 1 and 6 to 1 fold have been successfully prepared using peel oil to restore flavor to the product. These products have been prepared by adding cold pressed peel oil to concentrates just as they come from the evaporator, and excepting where sugar was added to adjust the sugar-acid ratio, nothing else was needed to prepare products of acceptable quality. In all cases sufficient oil was added to provide 0.007% (by volume) recoverable oil in the reconstituted juices.

A similar procedure produces both grapefruit and grapefruit-orange blends of comparable quality at 5 to 1 and 6 to 1 fold concentrations.

Samples of 6 to 1 concentrate have been placed in storage, and when compared periodically over a period of 6 months with equivalent 4 to 1 samples there has been no difference in flavor by statistical taste testing. Other samples are currently being tested for acceptance by the armed forces.

It can be shown that 6 to 1 fold concentrates possess several advantages over the conventional 4 to 1 products. For example: all evidence so far indicates less tendency to clarify and gel during temperature elevations; the higher concentrations are more easily reconstituted because they are not frozen as solidly at 0° F.; on the same equivalent fresh juice basis less refrigeration is required to reduce the temperature of the product; fewer containers are required (only 2 cans are needed for a 6 to 1 where 3 cans are used for a 4 to 1); and less product must be handled, stored and shipped.

Publications:

Flavor Fortification of California Frozen Orange Concentrate. R. G. Rice, G. J. Keller, and E. A. Beavens. Food Technology, 6(1):35-39, Jan., 1952.

STATUS OF TEXAS CITRUS PROCESSING INDUSTRY AND RESEARCH

by
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U. S. Fruit and Vegetable Products Laboratory
Weslaco, Texas

A year ago I presented to you a rather dark picture of the Rio Grande Valley following the disastrous freezes. The ensuing twelve months have brought to light nothing to improve the prospect. Planting has been slow due to shortage of nursery stock, to profitable use of land for cotton, feed, and vegetable crops, and the desire of owners to improve the land for most efficient drainage and irrigation before replanting. Water scarcity also has prevented replanting in the spring of 1952.

As forecast last year, production of fruit amounted to less than half a million boxes during the past season. We anticipate no more than a million boxes in 1952-53, with perhaps five million boxes being reached by 1955-56. Plantings will probably be in the neighborhood of one million trees a year, predominantly Ruby Reds.

First problem facing the processing industry when fruit again becomes available will be the utilization of red fruit in single strength canning. Normal commercial methods of canning and storage have resulted in an unattractive, muddy-appearing juice. Such juice once brought a premium merely because it was labeled as being from red grapefruit, but in only a few markets is it still acceptable even at a price equal to that from white juice.

Three methods of approach to the problem have been considered in our research program. The first and simplest method is the removal of color-bearing suspended matter. Mild centrifuging of normally extracted juice, plus blending with as little as 10 percent pulpy white juice, will give an attractive juice barely distinguishable from that of white grapefruit.

The second method of approaching the problem has been that of adding color. This is not as simple as it might sound, as the certified food colors from coal tar and the vegetable colors we have tried have all faded when stored in tin cans. Although colors hold fairly well in enameled cans, flavor of the juice deteriorates. The addition of color would probably not be acceptable to the Food and Drug people, nor to the industry, because it would permit competition from uncolored fruit.

The third and most difficult method of approach has been to try to retain full color of fresh juice. Red coloring matter of Foster Pink and Marsh Pink was identified by Matlack in 1935 as lycopene. We undertook to repeat his work for three reasons: literature revealed no corroboration of his studies; new varieties needed checking to prove assumption that color is the same, and a method will be required for quantitative studies of color contents in future seasons when fruit supplies become more plentiful.

Since lycopene is insoluble in aqueous media, it lends color to juice only when attached to suspended solid matter. Methods of recovering color from finisher wastes and dispersing it in screened juice are being tried, but have not yet proved successful.

Lack of fruit forestalls possibility of a concentrated juice industry in the Valley for some years to come. However, our investigations have been continued on a limited scale. Gelation and loss of cloud in unpasteurized concentrate continue to appear less of a problem than in Florida. There is no need to sweeten grapefruit concentrate, and concentrate from pink and red fruit holds its color perfectly for at least two years. Hot-pack concentrates for storage at refrigerator temperatures have not proved very successful, but we feel that definite progress has been made.

RESEARCH RELATED TO CITRUS PRODUCTS AT WESTERN REGIONAL RESEARCH LABORATORY, ALBANY, CALIFORNIA

Dr. John R. Matchett, Asst. Chief,
Bureau of Agricultural and Industrial Chemistry,
Washington, D. C.

The Carotenoids in Valencia Orange Juice

by
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There is evidence that the off flavor which develops on storage of canned or powdered orange juice may originate, at least in part, in the lipid (fat) fraction. Our ultimate objective is to isolate the individual lipids in the same form that they occur in the juice, and determine their roles in the development of off flavor. The initial work has been on one fraction of the lipids, the carotenoids, which are the principal pigments of orange juice. Several of the carotenoids have Vitamin A activity.

In Valencia orange juice the lipid fraction amounts to about 0.06 percent; the carotenoids are about 2 to 3 percent of the lipids, or around 0.0015 percent of the juice. Saponification of the lipid fraction removes about 70 percent of the non-carotenoids (fats, phospholipids, etc.), and converts the carotenoid esters (which amount to about 3/4 of the total carotenoids) to alcohols.

We have been studying the separation of the carotenoids of Valencia orange juice using a 100-tube Craig countercurrent distribution apparatus. With the saponified material, a clean-cut separation into 4 main fractions has been accomplished. These are apparently hydrocarbons, alcohols, diols and polyols. By the use of the Craig machine the diol fraction has been partially separated into 3 components, the polyol fraction into 4. Chromatography of the hydrocarbon fraction indicated the presence of four constituents, three of which have been tentatively identified by their absorption spectra as alpha, beta, and zeta carotenes. The absorption curve for the alpha carotene fraction indicated the presence also of phytofluene, a colorless fluorescent polyene. The alcohol fraction has been separated chromatographically into two components, one of which appears to be cryptoxanthin. Similarly the diol fraction has been shown to contain at least six constituents. The work so far has indicated the presence of at least seventeen constituents in the saponified carotenoid fraction.

Expansion of the 100-tube Craig apparatus to 200 tubes, which is in progress, should be very helpful in further resolving the carotenoid mixture.

Rapid Heat Processing of Fluid Foods by Steam Injection

by
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Albany, California

Work was undertaken to improve existing methods for the short-time, high-temperature, heat processing of fluid foods such as fruit and vegetable juices and purees. Pasteurization, sterilization, enzyme inactivation, deodorization, volatile flavor stripping, and/or concentration without impairment of quality were among the results sought.

A processing system, incorporating direct steam injection heating, has been developed and tested on a pilot plant scale. The injection heater will heat fluids to 300° F., or more in 0.5 second or less at practical processing rates. With the entire system, fluid foods may be heated to 300° F., concentrated, and cooled by vacuum evaporation in elapsed times of less than 1 second. Flavor changes have been insignificant when several fruit juices and milk were heat-processed to attain desired results.

The evaporating section of the processing system shows high resistance to fouling of heat transfer surfaces, and high heat transfer coefficients. With fruit juices and berry-sucrose puree (30% solids), overall heat transfer coefficients of 500 to 600 btu/hr.-sq.ft.-°F. were obtained in the evaporator.

Promise shown by the single-pass, rapid evaporator justified further development of the equipment. In consequence, an evaporator with 8 times the capacity of the initial model has been constructed and is under test. To date, performance of the large evaporator exceeds that of the small evaporator by a considerable margin.

Three commercial-scale installations have been made as a result of this work, and have successfully processed tomato juice, apple juice, and pear puree. However, performance of both pilot plant units exceeds that of the commercial installations, indicating the need for further development work for translating the equipment from pilot plant to commercial scale. Suitability of the equipment under development also remains to be determined for the processing of a variety of products, particularly those difficult to process, such as citrus juices and purees.

Publications:

Flash Heat. A. H. Brown, M. E. Lazar, T. Wasserman, W. D. Ramage. Food Packer 32(1), 20 (1951) and 32(2), 34 (1951).

Rapid Heat Processing of Fluid Foods by Steam Injection. A. H. Brown, M. E. Lazar, T. Wasserman, G. S. Smith, M. W. Cole. Ind. Eng. Chem. 43, 2949 (1951).

FACTORS AFFECTING THE FLAVOR OF CONCENTRATED CITRUS JUICES

by
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Florida Citrus Experiment Station
Lake Alfred, Florida

Frozen concentrated orange juice, since its commercial production began in 1946, has been a high quality, standardized product, retaining the flavor and nutritional characteristics of fresh fruit. Also from the consumer's point of view it is convenient to handle, reasonable in price, and available throughout the year. These are the reasons why more oranges are being utilized each year by citrus concentrators.

The continued acceptance and increased consumption of concentrated citrus juices, either frozen or heat-treated, will depend upon the maintenance of good flavor quality in these products. Anything that results in a lowering of the flavor quality in citrus concentrates will be detrimental to the sale of these products upon which total crop utilization depends today.

There are many factors that will affect the flavor of concentrated citrus juices. Such factors may be listed in three groups, (a) fruit factors, (b) processing factors, and (c) storage factors.

The flavor quality of most processed food products, whether fruit, vegetable, or meat, is dependent upon the flavor quality of the raw or fresh product used. Good flavor quality in orange concentrate will not result if poor quality oranges are used. The variety of fruit used, as well as its degree of maturity, will influence the flavor that results in the concentrated juice. The use of fruit internally infected with mold or bacteria will result in a finished product of poor quality.

Processing procedures affect flavor quality of citrus concentrates. Fruit should be processed as soon as possible after it has been harvested. Juice extraction and finishing procedures, resulting in excessively high juice yields, will extract substances from the fruit that will lower the flavor quality of the concentrated juice. Experimental results have indicated that portions of citrus fruit, other than the juice from within the juice sacs, will affect flavor of concentrate. Inclusion in the product of excessive amounts of peel oil, peel and rag extractives, or seed extractives are detrimental to the final flavor quality.

The use of heat treatment prior to, during, or after concentration of citrus concentrate will result in flavor changes in the product, the magnitude of the flavor change being dependent upon such factors as temperature used, heating time, type of equipment used, portions of whole fruit that are in the juice, and also others. Heat treatment can be used to inactivate pectic enzymes, that cause such objectionable changes as clarification and gelation, but sufficient experimental data are not yet available to indicate that this may be done without at the same time causing flavor changes that will result in products of lower flavor quality than that of frozen citrus concentrate made from juice that has not been heat treated. Heat treatment of juice prior to evaporation may also be used to destroy bacteria that can grow in juice in evaporators during the initial stages of concentration and thereby produce such off flavors that the product must be discarded.

Flavor deterioration that may take place in citrus concentrates during storage is caused chiefly by either chemical or microbiological changes. Temperature of storage is the most important factor in controlling these changes; however, the storage time is also significant. Heat-treated concentrates for storage at 40° F. must be more stable to all types of changes than frozen citrus concentrate provided the frozen product is stored continuously at 0° F. or below. It has not yet been proven that flavor changes during storage at 0° F. or higher temperatures are caused either by enzymes normally present in the juice of by enzymes produced from bacterial growth. Physical changes, gelation and clarification, occur in frozen citrus concentrates when these products are not stored properly, but it is doubtful that the pectic enzyme, pectinesterase, that causes these changes will bring about any flavor deterioration.

Research projects are underway at the Citrus Experiment Station, Lake Alfred, Florida, that should result in experimental data that will be of assistance in solving some of the present unanswerable questions concerning the many factors that may affect the flavor of concentrated citrus juices.

IMPROVEMENT OF QUALITY OF SINGLE-STRENGTH JUICES

by
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Dr. P. Phillips Companies
Orlando, Florida

There is an old saying that you can't make a silk shirt out of a sow's ear, neither can you make good juice out of poor fruit.

There is a great deal of single-strength juice canned early from packing house eliminations. That is to say, fruit that did not come up to fresh fruit standards is processed into single-strength juice. Most of this fruit goes through ethylene gas chambers anywhere from 42 to 72 hours. The fruit is graded out from the packing house operations and conveyed into a canning grade bin. The following day, the fruit is moved to a processing plant and probably it stays in the bins of the processing plant another day, and by the time the juice is extracted and processed the flavor isn't very good. In fact, I have tasted juice in which I could detect the ethylene gas from the coloring rooms.

I would say that a large percentage of fruit processed after the 1st of December is of a very good quality when first canned, but the juice is pasteurized from temperatures of 185° - 200° F., then cooled down to 90° - 125° depending on the facilities to properly cool the cans at the various plants. The reason for leaving the juice at these temperatures is apparently to dry off the moisture from the tin cans, so that they won't rust, but after the labels are applied, the cans are packed into corrugated cartons and stacked closely together in a warehouse where it takes about thirty days for the merchandise to cool down to room temperature. A great deal of damage is done to the juice on account of the slow cooking it receives during the thirty days period. In my opinion, the juice could be cooled down to lower temperatures after closing, say to 70°, using mechanical refrigeration to do it, and mechanically drying the cans rather than having to depend on internal heat to dry them off.

A new extracting machine has recently been developed which is a very efficient machine, but in my opinion, many operators are trying to get too much yield out of a box of fruit. I believe that the quality of single-strength juice could be improved by letting up a bit on this extracting operation, thereby getting a slightly lower yield but improvement in the flavor. You understand, I am not condemning the machine, I am simply condemning the misuse of the machine in some instances.

Another thing, canned goods are sometimes stored in Florida in hot warehouses in the summer months during which time the temperatures are all the way from 85° - 100°, and this too is injurious to the flavor. It is very desirable to maintain temperatures at around 70° during summer storage. This can be done by properly insulating the warehouse and installing mechanical refrigeration if necessary to do the job. This will go a long way in retaining good flavor in the products.

FLAVOR CHANGES IN CANNED SINGLE-STRENGTH ORANGE JUICE DURING STORAGE

by
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Winter Haven, Florida

By way of introduction, past work at the Winter Haven Station and elsewhere is reviewed to give background material for the new work presented. In this part of the talk, the possible mechanisms that cause the sharp, characteristic flavor to develop in orange juice on storage are discussed. Among these explanations are the inclusion of oxygen when the cans are closed, changes in peel oil, and changes in the lipid fraction. The first of these, the inclusion of oxygen, has been generally eliminated as a cause. Some conflicting opinions have been expressed with regard to peel oil. It is generally considered a necessary and desirable flavor constituent of fresh juice, but is considered by many to be the origin of the characteristic storage off-flavor. Among the explanations of this phenomenon is the belief that the d-limonene changes to the l-form, to 1,4-cineole, or to carvone and carveol. As to the role of the lipid, earlier work in the Winter Haven Laboratory showed that this substance gave rancidity reactions when isolated from aged juice. More recently, the lipid has been analyzed and different fractions of it added to whole juice, filtered juice, and synthetic juice in an effort to identify what part, if any, was responsible for the typical off-flavor. These experimental packs were stored at 35° F. and 80° F. for varying periods and included additions of phosphatides, ethanolamine, choline, whole peel oil, 10-fold peel oil, and terpeneless peel oil and are briefly reviewed here, having been covered in previous talks.

The results of new work on synthetic juice are given. Additions have been made of the whole lipid, lipid unsaponifiable matter, lipid fatty acids, lipid volatile, carotene, d-limonene, d-limonene plus carotene, and the volatile peel oil constituents. The results of these experiments indicate that some constituent of the peel oil, possibly the d-limonene, plays an important role in the production of the characteristic off-flavor. However, this conclusion is complicated by the fact that whole juice deteriorates much faster and more profoundly than does filtered juice or synthetic juice containing the same amount of peel oil. Hence, it seems likely that the lipid matter may exert much influence. Possibly, the suspended matter of whole juice simply keeps the peel oil dispersed and thus enhances its effect by maintaining contact.

RECOVERY OF ESSENCE FROM CITRUS JUICES

by
D. A. Morgan and M. K. Veldhuis
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Winter Haven, Florida

Adaptations of the essence recovery equipment developed by the Eastern Regional Research Laboratory for apples, grapes, and other fruits have been tried on citrus fruits.

The first work done at this laboratory stripped the orange juice at atmospheric pressure. A water soluble, aromatic material, designated here as essence, as well as a peel oil fraction were obtained. However, the times and temperatures used to strip the orange juice of aroma were too drastic for heat sensitive materials and the orange juice developed a cooked flavor.

In recent work at this laboratory a vacuum system has been used which was also developed at the Eastern Regional Research Laboratory. The orange juice was stripped at 110-115° F. Vapors were condensed, the peel oil decanted and the aqueous layer revaporized. A product was obtained by fractionation of the latter vapors in a packed column. All vent lines led to a manifold, and exit gases were scrubbed with cold fractionating column bottoms. The liquid used for scrubbing was mixed with condensed vapors from the first vaporization and recycled. All gases and vapors coming from the scrubber were passed through dry ice traps to condense additional vapors.

In operation, approximately 10 percent of the orange juice was vaporized. Of this 10 percent, approximately 6.5% was finally removed as product, giving an essence of about 150 fold.

The character of orange essence, like that of apple, is found to vary with the variety of citrus used. Pineapple oranges, Valencia oranges, tangerines, grapefruit and Meyer lemons each have a distinctive essence.

Essences of citrus fruits appear to be stable when stored in glass bottles at 35° F. Samples of Valencia orange essence prepared by atmospheric stripping were not noticeably different after five years storage from essences of the same variety of oranges recently prepared by vacuum stripping.

Orange essence, when added in normal amounts to orange concentrate, becomes organoleptically undetectable in the reconstituted juice after about six months of storage at 0° F. A residual effect noted was a heightening of the peel oil taste of the reconstituted juice.

The variation of strength of essence with oil content was also investigated. Juice was derived from the same lot of Pineapple oranges. The recoverable oil content of the whole fruit puree was 0.880 percent; of the machine extracted juice was 0.024 percent; of the hand reamed juice was 0.006 percent; and of the juice considered free of peel oil, 0.004 percent. In this last juice, the oranges were plumped in hot permanganate solution, and the permanganate finally removed by sulfite solution. The orange juice was then extracted from the orange balls.

The orange juices by these various methods of extraction were passed twice through the essence unit, essence and trap condensate being obtained for each pass. The fold of concentrations was calculated by dividing the amount of juice used by the sum of the volumes of the essence and trap condensate.

All essences and their corresponding trap condensates were adjusted to the same fold of concentration with distilled water. The adjusted essences and trap condensates were then rated by comparing the dilutions at which oder was last detected.

Comparing similar essences from different juices, it was found that the strength of the water soluble essences ranked with the oil content of the juice from which it was derived.

Comparing essences derived from consecutive passes, it was found that not all of the aroma is stripped in one pass of 10 percent vaporization. The essences of the second pass were approximately half the strength of the corresponding essences of the first pass.

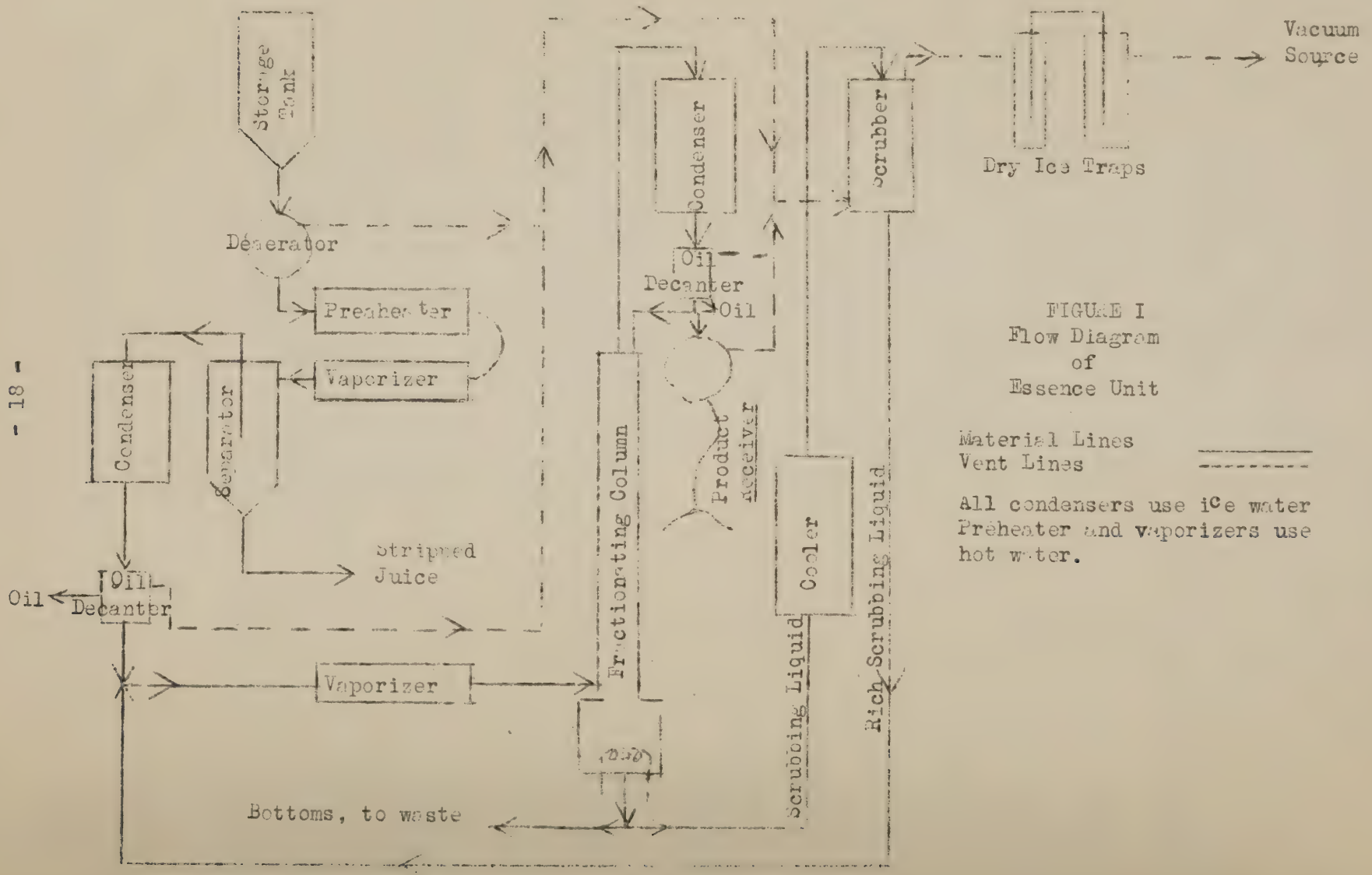

FIGURE I
Flow Diagram
of
Essence Unit

Material Lines ————————
Vent Lines - - - - - - - -

All condensers use ice water
Preheater and vaporizers use
hot water.

PECTIC SUBSTANCES IN CITRUS JUICES AND CONCENTRATES

by
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Because of the gelation problem in frozen orange concentrate, there has developed a need for a quick and simple method for determining pectin in citrus juice. S. M. Stark, Jr. of the Southern Regional Research Laboratory developed a colorimetric method for determining pectic substances in cotton fiber (Anal. Chem. 22, 1158, 1950). He based his work on that of Z. Dische, Jr. (Biol. Chem. 167, 189, 1947). E. A. McComb and R. M. McCready of the Western Regional Research Laboratory modified the method for determining pectic substances in fruit juices. This method has been applied to concentrated citrus juices and examples of the estimation of both total and soluble pectin are to be given.

The method depends on the decomposition of the pectic substances with concentrated sulfuric acid and the formation of a colored compound with carbazole and the decomposition products. The method is very sensitive, detecting and measuring pectic substances in microgram amounts. We have found this is the best method available for determining pectic substances in orange concentrate. It is faster and easier to run than the Carre' Haynes pectate method.

PROCEDURE

Extracting Pectic Substances from Orange Concentrate:

(1) Total Pectin - A 10 gram sample of concentrate (42° Brix) is weighed into a 50 ml. graduated centrifuge tube. A 25 ml. volume of ethyl alcohol is added, the juice and alcohol thoroughly mixed, allowed to stand a few minutes while the pectic substances precipitate, and then centrifuged for 10 min. at about 2000 R.P.M. The liquid is decanted and the precipitate and pulp washed twice with a 2-1 alcohol-water mixture. The precipitate and pulp are carefully broken up and suspended with each washing. After the last washing, the precipitate and pulp and taken up in about 60 ml. of water, 2 ml. of 10 percent versene added and the mixture heated for 45 min. on a steam bath. The solution is then diluted to 100 ml. in a volumetric flask and filtered. A 5 ml. aliquot of the filtrate is then diluted to 100 ml. in a volumetric flask. A 2 ml. aliquot taken for analysis by the carbazole method represents 0.01 grams of 42° Brix concentrate.

(2) "Soluble" Pectin - (Soluble pectin in this case may be defined as the pectin or pectic substances that is filterable through a No. 1 Whatman filter paper.) A 10 gram sample of orange concentrate (42° Brix) is weighed into a 50 ml. graduated centrifuge tube. The 10 grams of concentrate are then diluted to the 50 ml. mark of the centrifuge tube with distilled water and mixed well. It is then centrifuged and the serum filtered through a filter paper. A 15 ml. aliquot of the filtered serum is pippetted into a 50 ml. centrifuge tube and 35 ml. of alcohol is added. The alcohol and juice serum are mixed thoroughly and allowed to stand a few minutes. It is then centrifuged for 10 min. at about 3000 R.P.M. and the clear serum decanted from the precipitate. The precipitate is washed with a 2-1 alcohol-water solution, being careful to

break up the precipitate and suspend it in the wash solution. After the washing, the pectic substances are taken up in about 15 cc of .05 N sodium hydroxide, allowed to stand 30 min. at 25-30° C. and then diluted to 100 ml. volume. A 2 ml. sample taken for analysis by the carbazole method represents 0.06 grams of 42° Brix concentrate.

Reagents

Ethyl Alcohol, purified. Reflux 1 liter of reagent grade, 95 percent ethyl alcohol with 4 grams of zinc dust and 4 ml. of 1-1 sulfuric acid at least overnight (preferably 24 hours). Distill, using all-glass apparatur. Redistill from zinc dust and potassium hydroxide, using 4 grams of each to 1 liter of alcohol.

Carbazole, reagent grade recrystallized from toluene. Dissolve 150 mg. of the recrystallized carbazole in purified alcohol and dilute to 100 ml.

Sulfuric Acid, reagent grade.

Galacturonic Acid, monohydrate. Recrystallized from ethyl alcohol.

Development of Color - By means of a measuring pipette, calibrated to deliver 12 ml., pipette this volume of sulfuric acid, 95 percent, into a test tube (25 x 200 mm.). Immerse the tube (or tubes) in ice water until the temperature of the acid is ca. 3° C. Add accurately 2 ml. of the solution of pectic substances extracted from orange concentrate. Close the tube by inserting a 5 ml. beaker in the mouth and mix thoroughly. Replace the tube in the ice water and recool to ca. 3° C. Then heat for 10 minutes in a boiling water bath. Cool rapidly to ca. 20° C., add 1 ml. of a 0.1 percent solution of carbazole. Mix thoroughly and let stand -- read the color using a 520 mμ filter after ~~exactly one hour~~ 25 ± 5 minutes. The reading time is important and for this reason no more than 8 tubes should be carried through the procedure at one time and the carbazole should be added to all the tubes before any are mixed.

Preparation of a Standard Curve - Weigh accurately 100 mg. of galacturonic acid monohydrate into a 1 liter volumetric flask and made to volume. Take 5, 10, 15, 20, and 30 ml. aliquots and dilute to 100 ml. Two ml. of each of these dilutions will contain 10, 20, 30, 40, and 60 micrograms of G. A. Develop the color standard by treating 2 ml. aliquots as described for the sample solution. Two ml. of sample plus 12 ml. of concentrated sulfuric acid plus 1 ml. of purified ethyl alcohol should be run as a blank colorimeter setting; a blank of 2 ml. of water, 12 ml. sulfuric acid, and 1 ml. of carbazole solution should be carried through from time to time, it should have a transmittance of about 95 percent. For the standard curve, plot log transmittance against concentrations of anhydrogalacturonic acid. To obtain anhydrogalacturonic acid multiply the monohydrate by their molecular weight ratio, 176/212.

This method has been applied to a few samples of concentrates including some commercial lots. Some variations in total pectin have been noted, but the variations in soluble pectin have been much wider. These studies are continuing.

PROGRESS REPORT ON STORAGE OF FROZEN CONCENTRATE

by
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The study of storage temperature effects on frozen citrus concentrates was undertaken as a cooperative project between the Minute Maid Corporation and this laboratory in the 1949-50 season. Frozen concentrates of orange juice, grapefruit juice, tangerine juice, and blended orange and grapefruit juices were stored at -20°, -8°, 0°, 5°, 10°, 15°, 20°, 25°, 45°, and 75° F. The result of this cooperative study was published and reprints are available.

It is realized that seasonal variations are to be expected and variations in manufacturing practice undoubtedly result in variations in the product. Changes take place very slowly at low temperatures and it is at these temperatures that more information is desired. With these questions in mind the storage study is continuing here at the U. S. Citrus Products Laboratory in Winter Haven.

Last year the samples included the four largest producers in Florida. This year samples were secured from ten plants employing all types of equipment now in use.

The samples were secured in each case from the plant and transported to the laboratory with dry ice.

Facilities at this laboratory provide 35°, 20°, 15°, 10°, 5°, and 0° F., storage.

Analytical methods are much as described in the early publication except for the following: The concentrates are reconstituted to 12° Brix. Speed and refrigeration are employed to minimize time and temperature effects.

Gelation is recorded using the method suggested by the Citrus Experiment Station at Lake Alfred.

The pectinesterase activity is determined by the method suggested by Mr. Eugene F. Jansen of the Western Regional Research Laboratory. A description of the method is attached to this summary.

In the 1949-50 season no gelation was observed. In the 1950-51 season all samples gelled at 20° and 15°, but no gelation was observed at 10°, 5°, or 0° F. In the current, 1951-52, season some samples gel promptly under favorable conditions and other samples show no indication of gelation.

The cloud retention as measured by cloud index shows a great difference in the behavior of individual samples. While some samples are surprisingly stable it would be rash to consider storage specifications without regard for the most unstable samples. The lower storage temperatures promise to provide valuable information. The 35° F. accelerated storage charts the pattern for slower low temperature storage changes. The 35° F. storage approaches the treatment concentrate might receive in the household refrigerator.

So far there is noted a surprising variation between samples. The difference between samples is greater than the largest seasonal variation measured. The changes in the concentrate occur much more slowly at lower storage temperatures.

Interest has been indicated in the method used for pectinesterase assay. This is briefly described below.

Method of Measuring Pectinesterase Activity Suggested by Mr. Eugene F. Jansen

A 2-6 ml. aliquot of the reconstituted concentrate is placed in 20 ml. of 1 percent pectin solution containing .25 M sodium chloride. The pH is brought to 7.5 with 0.1N sodium ~~chloride~~ hydroxide. Distilled water is added so that the total volume is about 40 ml. The assay vessel is placed in a constant temperature bath at 30° C. Agitation is provided by a stream of air from which carbon dioxide is removed. Caprylic alcohol is used to eliminate foaming.

The technique is to bring the pH to just above 7.5. As the pH comes down through 7.5 the time is recorded. Successive additions of 0.02N sodium ~~chloride~~ hydroxide each bringing the pH just above 7.5 provide readings of time and volume of alkali. This is continued until the graph of volume and time provides the slope of a straight line or until the number of gram milliequivalents per minute is practically constant. The size of the aliquot for analysis is usually 2 ml. but more may be used if the pectinesterase activity is low. The amount of enzyme is chosen sufficient to require 1-3 ml. of 0.02N sodium ~~chloride~~ hydroxide in 10 minutes.

Results are expressed in pectinesterase units (PEu)ml. which represents the milliequivalents of ester hydrolyzed per minute per milliliter of reconstituted concentrate under the conditions specified above. Since these units are very small it is convenient to tabulate them in terms of (PEu)ml. times 10^4.

EFFECTS OF PROCESSING AND STORAGE TEMPERATURES ON VALENCIA ORANGE CONCENTRATES

by
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Frozen citrus concentrates are not pasteurized and as brought out by DuBois and Kew (Refrig. Engin. 59, 772, 1951) are not stable above 0° F. In some cases storage at this low temperature is not available and it would seem desirable, if practicable, to develop concentrates which would be stable at a higher temperature.

The object of these experiments was to determine the effect of several levels of heat treatment on orange juices of different concentrations.

Single strength, two-fold, four-fold, and six-fold products were prepared from Valencia orange juices, subjected to heat treatments of 120°- 200° F. in 10° F. steps, canned hot and cooled under water sprays. Reference, unheated samples were also prepared. Representative samples were placed in 0°, 35°, and 80° F. storage.

Methods of evaluation included pectinesterase activity, cloud stability, and bacteriological plate counts.

The data indicated a regular decrease in pectinesterase enzyme activity with increased treatment temperature in the range of 120 -160° F. Treatments of 160° F. inactivated 89-95 percent of the pectinesterase originally present. There was little change in the residual activity with increased treatment temperatures from 160° up to and including 180° F., representing inactivations of 94-96 percent of the enzyme. Heat treatments of 190° F. inactivated 97 percent or more while 200° F. was responsible for not less than 98 percent pectinesterase enzyme inactivation. Under the conditions of the experiment there would appear to be little advantage in heating to 180° over that of 160° F.

Plate counts on Lindegren's Agar indicated decreasing numbers of organisms with increasing treatment temperatures up to 150° F. With treatments of 160° F. and above there were further reductions, but the differences were not so great.

The degradation of the cloud in the experimental products, evaluated as a function of time in 35° F. storage, indicated that stability was not attained by treatments of 140° F. or less. Treatments of 160° to 180° F. were sufficient to stabilize the cloud in six-fold products only, while heating to 190° and 200° F. effected cloud stabilization in all products regardless of concentration.

It was observed that although enzyme inactivation appeared of a similar order for any given heat treatment regardless of concentration, cloud stability was attained in six-fold concentrates at lower processing temperatures than were required for less concentrated juices.